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SLOW DYNAMICS OF NONEQUILIBRIUM DENSITY FLUCTUATIONS IN CONCENTRATED COLLOIDAL SUSPENSIONS

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The principal purpose of this work is to study the dynamics of nonequilibrium density fluctuations in concentrated hard-sphere suspensions of interacting Brownian particles with both hydrodynamic and direct interactions, and thus to explore the slow relaxation process in colloidal glasses. A well-known example of this kind is the so-called mode-coupling theory (MCT), which was proposed by Bengtzelius, Götze, and Sjölander and , independently, by Leutheusser [1]. Although this theory was the origin of all later experimental, theoretical, and numerical studies of colloidal glasses [2], we find two unsatisfactory points in their basic viewpoints. First, MCT is valid only for equilibrium systems. In general, however, most experimental measurements on quenched colloidal suspensions are done in a metastable fluid state prior to crystallization. Hence the nonequilibrium effects may change the behavior of relaxation processes. Secondly, MCT contains a number of adjustable parameters. However, it has not been addressed yet to understand those parameters physically from a microscopic point of view. Thus, it might be still one of fundamental problems in statistical physics to formulate a new scheme for finding stochastic equations for nonequilibrium density fluctuations in concentrated colloidal suspensions.

The first problem above suggests that one must derive a nonlinear diffusion equation for the average number density $n(\boldsymbol{x},t)$ in order to discuss the diffusion process in nonequilibrium states. This was recently done by the present author and Oppenheim [3]. The alternative diffusion equation for $n(\boldsymbol{x},t)$ was derived, from which the short- and long-time self-diffusion coefficients, $D_S^S(\phi)$ and $D_S^L(\phi)$, are obtained self-consistently, where ϕ denotes the volume fraction of the particles. The second problem requires us to derive a stochastic equation for the fluctuations $\delta n(\boldsymbol{x},t)$ around the average number density $n(\boldsymbol{x},t)$. Then, the coupled equations for $n(\boldsymbol{x},t)$ and $\delta n(\boldsymbol{x},t)$ must be solved self-consistently to study the diffusion process in metastable fluid state. Thus, the parameters contained in the theory will be understood physically from a microscopic point of view. In this paper, I first propose such coupled equations and then investigate the asymptotic behavior of the slow relaxation processes of the nonequilibrium density fluctuations in concentrated colloidal suspensions.

We discuss a suspension-hydrodynamic stage of a colloidal suspension which consists of N identical spherical particles with radius a_0 and an incompressible fluid with viscosity η_0. In this stage the space-time cutoffs (x_c,t_c), which are the minimum wavelength and time of the dynamic process of interest, are set as $x_c \gg \ell$ and $t_D \gg t_c \gg t_B$, where ℓ denotes the screening length given by $\ell=(6\pi a_0 n_0)^{-1/2}$, in which the hydrodynamic interactions becomes important, $t_B \sim m/(6\pi\eta_0 a_0)$ the relaxation time of the sphere, and $t_D \sim \ell^2/D_S^S$ the structural-relaxation time, which is a time required for a particle to diffuse over a distance ℓ. Here n_0 is the equilibrium number density of the spheres.

As was shown in the previous paper [4], the nonequilibrium density fluctuations obey a linear stochastic equation

$$\frac{\partial}{\partial t}\delta n(\boldsymbol{x},t) = \nabla^2[D_S(\Phi(\boldsymbol{x},t))\delta n(\boldsymbol{x},t)] + R(\boldsymbol{x},t) \tag{1}$$

with the self-diffusion coefficient

$$D_S(\Phi) = D_S^S(\phi)\frac{(1-u\Phi/\phi_0)}{1+d_S(\phi)K(\Phi)}, \tag{2}$$

where $R(\boldsymbol{x},t)$ denotes a Gaussian, Markov random force and satisfies

$$\langle R(\boldsymbol{x},t)\rangle = \langle R(\boldsymbol{x},t)\delta n(\boldsymbol{x}',0)\rangle = 0, \tag{3}$$

$$\langle R(\boldsymbol{x},t)R(\boldsymbol{x}',t')\rangle = -2\delta(t-t')\langle \delta n(\boldsymbol{x}')^2\rangle \nabla^2[D_S(\Phi(\boldsymbol{x},t))\delta(\boldsymbol{x}-\boldsymbol{x}')]. \tag{4}$$

The brackets denote the average over the canonical ensemble. Here $u = 9\phi_0/32$ and $d_S(\phi) = D_S^S(\phi)/D_0$, where $\phi = 4\pi a_0^3 n_0/3$ and D_0 are the volume fraction of particles and the single-particle diffusion coefficient, respectively. The critical volume fraction ϕ_0 is given by $\phi_0 = (4/3)^3/(7\ln 3 - 8\ln 2 + 2)$. $D_S^S(\phi)$ indicates the short-time self-diffusion coefficient (see Ref.[3] for details).The term $K(\Phi)$ in Eq.(2) represents the correlation effect due to the nonlocal long-range hydrodynamic interactions and is given by

$$K(\Phi) = \frac{\Phi/\phi_0}{(1-\Phi/\phi_0)^\kappa}, \tag{5}$$

where $\kappa = 2$ here. This becomes singular at $\Phi = \phi_0$ and describes a cage effect which causes a structural arrest in the relaxation of density fluctuations. Finally, the function $\Phi(\boldsymbol{x},t)$ denotes the local volume fraction given by $\Phi(\boldsymbol{x},t) = \phi\, n(\boldsymbol{x},t)/n_0$ and obeys the nonlinear deterministic equation

$$\frac{\partial}{\partial t}\Phi(\boldsymbol{x},t) = \nabla\cdot[D_S(\Phi(\boldsymbol{x},t))\nabla\Phi(\boldsymbol{x},t)]. \tag{6}$$

This equation describes a causal motion of self-diffusion processes in nonequilibrium states of concentrated hard-sphere suspensions.

For the short-time region where $t_B \ll t \ll t_D$ and $|\boldsymbol{x}| \ll \ell$, the coupled effect $u\Phi(\boldsymbol{x},t)$ and the cage effect $K(\Phi)$ are negligible. In this region, therefore, the self-diffusion coefficient $D_S(\Phi)$ reduces to the short-time self-diffusion coefficient $D_S^S(\phi)$. After this region, both effects become important. For the long-time region where $t \gg t_D$ and $|\boldsymbol{x}| \gg \ell$, $D_S(\Phi)$ reduces to the long-time self-diffusion coefficient $D_S^L = D_S(\phi)$, which vanishes quadratically as $D_S^L \sim 0.84D_0(1-\phi/\phi_0)^2$ near ϕ_0 because of the cage effect $K(\phi)$. Thus, the coupled equations (1) and (6) describe crossover behaviors between the short-time region and the long-time region.

In order to discuss the relaxation process of nonequilibrium density fluctuations around the metastable state, one must solve the coupled alternative diffusion equations (1) and (6) self-consistently. In the following, however, we discuss only the single-mode behavior of the number density $n(\boldsymbol{x},t)$ with the length scale of order L. This leads to $n(\boldsymbol{x},t) = n_0 z(t/t_\gamma;L)$, where $z(0;L) = z_0$ and $z(\infty;L) = 1$. In fact, by putting $|\nabla| \sim (2\pi/L)$ and $t_\gamma = (L/2\pi)^2/D_S^S$, one can solve Eq.(6) approximately as $z(t) = (z_0 + t)/(1+t)$. By taking a Fourier transformation of Eq.(1) and introducing the dimensionless variables by $q = ka_0$, $\tau = D_0 t/a_0^2$ and $\tau_\gamma = D_0 t_\gamma/a_0^2$, we thus obtain the

self-intermediate-scattering function given by $F_S(k,t) = <\delta n(k,t)\delta n(-k,0)> / <|\delta n(k,0)|^2>$, where $\delta n(k,t)$ denotes a Fourier component of the density fluctuations $\delta n(x,t)$. Figure 1 shows the time dependence of the scattering function $F_S(k,t)$ for different volume fractions ϕ at $z_0 = 0.8$, where $q = 2.8$ and $kL = 2\pi$. For small volume fractions the scattering functions decay quickly to zero. As the volume fraction increases, the shape of $F_S(k,t)$ becomes very sensitive to volume fraction, leading to a formation of a shoulder. In Fig.2 we also plot the dynamic susceptibility given by $\chi_S''(q,\omega) = \omega \int_0^\infty \cos(\omega\tau) F_S(q,\tau) d\tau$ for different volume fractions ϕ at $z_0 = 0.8$. In Fig.2 we clearly see that there are two peaks and one minimum in χ_S''; the first peak at $\omega = \omega_\alpha = q^2 D_S^L / D_0$ in the lower frequency region, the second peak at $\omega = \omega_\gamma = q^2 D_S^S / D_0$ in the higher frequency region, and the minimum at $\omega = \omega_\beta$ in between the first and the second peaks, where $\omega_\alpha < \omega_\beta < \omega_\gamma$. The characteristic frequencies ω_α, ω_β, and ω_γ are then shown to be scaled with the separation parameter $\sigma = \phi/\phi_0 - 1$ as $\omega_\alpha(\sigma,q) \propto |\sigma|^2$, $\omega_\beta(\sigma,q) \propto |\sigma|^\beta$, where $\beta = 1.33$ ($z_0 = 0.8$) for $\sigma \le 0$. Thus, there are two different slow relaxations, α and β relaxations,concerned with ω_α and ω_β in the fluid state ($\sigma < 0$) near ϕ_0. Hence the relaxation proceeds in the following four time stages for $\phi < \phi_0$ ($\sigma < 0$)

[E] early stage where $\tau_B \ll \tau \ll \tau_\gamma$ ($\omega_\gamma \ll \omega \ll \omega_B$);

$$F_S^S(q,\tau) = \exp(-q^2 d_S \tau), \qquad \chi_S''^S(q,\omega) = q^2 \omega d_S / (\omega^2 + q^4 d_S^2), \tag{7}$$

[β] β-relaxation stage where $\tau_\gamma \ll \tau \ll \tau_\beta$ ($\omega_\beta \ll \omega \ll \omega_\gamma$);

$$F_S^\beta(q,\tau) = f_q^c - A_q(\tau/\tau_\beta)^a, \qquad \chi_S''^\beta(q,\omega) = A_q''(\omega/\omega_\beta)^a, \tag{8}$$

[α] α-relaxation stage where $\tau_\beta \ll \tau \ll \tau_\alpha$ ($\omega_\alpha \ll \omega \ll \omega_\beta$);

$$F_S^\alpha(q,\tau) = f_q^c - B_q(\tau/\tau_\alpha)^b, \qquad \chi_S''^\alpha(q,\omega) = B_q''(\omega/\omega_\alpha)^{-b}, \tag{9}$$

[L] late stage where $\tau_\alpha \ll \tau$ ($\omega \ll \omega_\alpha$);

$$F_S^L(q,\tau) = \exp[-q^2 d_L \tau], \qquad \chi_S''^L(q,\omega) = q^2 \omega d_L / (\omega^2 + q^4 d_L^2), \tag{10}$$

where $\tau_i = 2\pi/\omega_i$, ($i = \alpha, \beta, \gamma$), and the positive constants A_q, A_q'', B_q and B_q'' are weak functions of ϕ and z_0. As predicted by MCT [1], for intermediate times, there are two types of power-law decays; the first decay towards a plateau in stage [β] and the von Schweidler decay in stage [α]. However, the time exponents a and b depend on ϕ and z_0. We also mention that when the system is in equilibrium, the two slow relaxations disappear and the late stage [L] only exists. These situations are quite different from those of MCT.

In summary we have studied the dynamics of nonequilibrium density fluctuations in concentrated hard-sphere suspensions. We have shown that the nonequilibrium effect changes the qualitative behavior of relaxation processes. In fact, in nonequilibrium states the two different slow relaxations are caused by the cage effect $K(\Phi(x,t))$ given by Eq.(5), while in equilibrium states they disappear. This situation is quite different from MCT. The detailed properties of slow relaxations could be obtained by solving the coupled equations (1) and (6) self-consistently, where the initial value $\Phi(x,0)$ is only the adjustable parameter. This will be discussed elsewhere.

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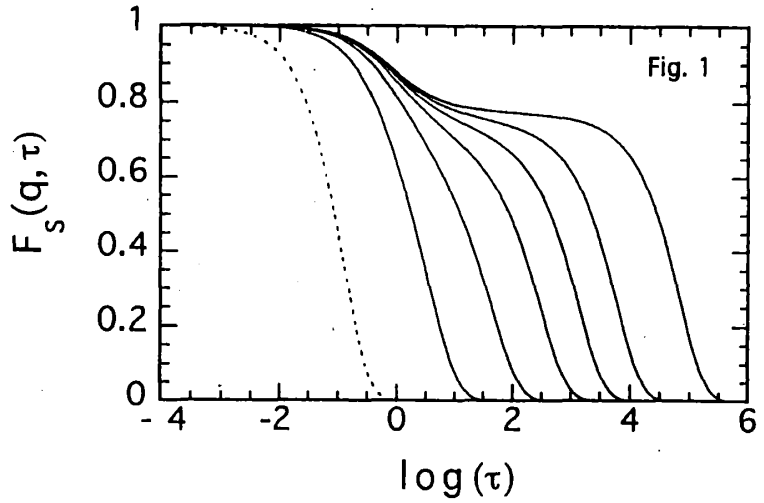

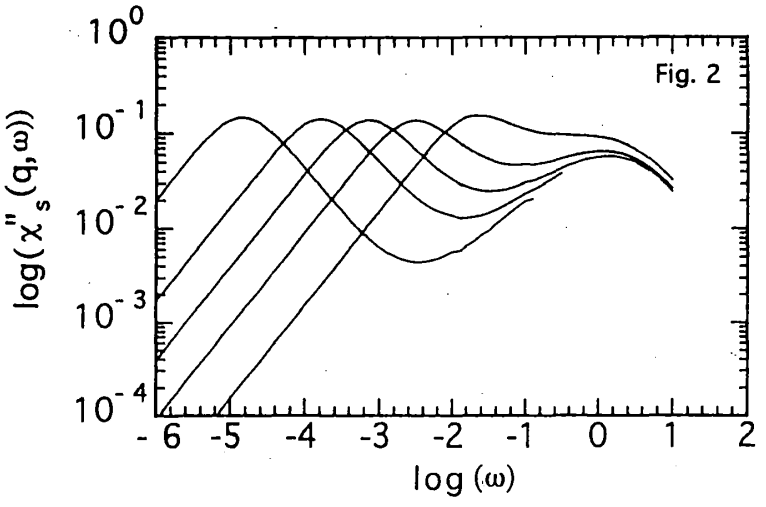

Fig.1. Self-intermediate-scattering function $F_S(k,t)$ vs t at $q = 2.8$ and $z_0 = 0.8$ for different volume fractions (from left to right): 0.480, 0.543, 0.560, 0.566, 0.569, 0.571. The dotted line indicates the function $F_S(k,t)$ for $\phi = 0.0$.

Fig.2. Dynamic susceptibility $\chi''_S(k,\omega)$ vs ω at $q = 2.8$ and $z_0 = 0.8$ for different volume fractions (from right to left at lower frequency side): 0.543, 0.560, 0.566, 0.569, 0.571.